FORM PTO 1390 (REV 11-2000) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		HUBR-1207
		U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/088712
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATES	PRIORITY DATE CLAIMED
PCT/EP00/09587	29 September 2000	29 September 1999

SULFONATED CONDENSATION PRODUCTS WHICH ARE STABILE IN STORAGE, METHOD FOR THE PRODUCTION THEREOF, AND THEIR USE

APPLICANT(S) FOR DO/EO/US **Uwe HOLLAND, et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [x] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing 35 U.S.C. 371
3. [X] This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [ ] The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371 (c)(2))
   a. [X] is attached hereto (required only if not communicated by the International Bureau).
   b. [X] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)).
   a. [X] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. [X] An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [X] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [X] Other items or information: PCT/ISA/210; PCT/IPEA/409

U S APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/088712	PCT/EP00/09587	HUBR-1207

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) – (5)):

		CALCULATIONS PTO USE ONLY
[ ]	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO And International Search Report not prepared by the EPO or JPO $1040.00	
[X]	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO $890.00	
[ ]	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO $740.00	
[ ]	International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) $710.00	
[ ]	International preliminary examination fee (37 CFR 1.482) paid to USPTO And all claims satisfied provisions of PCT Article 33(1)-(4) $100.00	

ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00	
Surcharge of $ _____ for furnishing the oath or declaration later than [ ] 20 [X] 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	-20 =	0	X	$	
Independent claims	1-3 =	0	X	$	
MULTIPLE DEPENDENT CLAIM(s) (if applicable)			X	$	
TOTAL OF ABOVE CALCULATIONS =				$ 890.00	
[ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above Are reduced by ½.				$	
SUBTOTAL =				$ 890.00	
Processing fee of $ _____ for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				$	
TOTAL NATIONAL FEE =				$ 890.00	
Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment Must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) (per property). +				$ 40.00	
TOTAL FEES ENCLOSED =				$ 930.00	
				Amount to be Refunded:	$
				Charged:	$

a. [X] A check in the amount of $ $930.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. _____ in the amount of $ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to my Deposit Account No. 50-0624 . A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

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25145314.1

HUBR-1207 (10202926)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s)	:	Uwe HOLLAND, et al.
Serial No.	:	To be assigned
Filed	:	Herewith
For	:	STORAGE-STABLE SULFONATED CONDENSATION PRODUCTS, PROCESS FOR PREPARING THEM AND THEIR USE
Art Unit	:	To be assigned
Examiner	:	To be assigned

March 20, 2002

Commissioner of Patents
and Trademark
Washington, D.C. 20231

I hereby certify that this correspondence is being deposited with the United States Postal Service by Express Mail in an envelope addressed to Commissioner of Patents and Trademarks, Washington, D.C. 20231 on March 20 2002

Eileen Sheffield Eileen Sheffield 3/20/02
Signature Date

PRELIMINARY AMENDMENT

Prior to examination, please amend the above-identified patent application as follows::

IN THE CLAIMS

Cancel claims 1-12 without prejudice and add the following new claims:

13 A storage-stable sulfonated condensation product based on an amino resin former having at least two amino groups, at lest one of sulfite and naphthalenesulfonic acid; and formaldehyde and, optionally organic nitrogen bases, comprising: at least one nitrogen-containing formulation auxiliary selected from the group consisting of a compound of formula)

$$R^1\text{-NH-X-Y-}R^2 \qquad (1)$$

wherein

R^1 and R^2 are independently H, $-CH_3$, $-C_2H_5$, $-C_3H_7$ or together form $-CH_2)_n-CH_2-$;

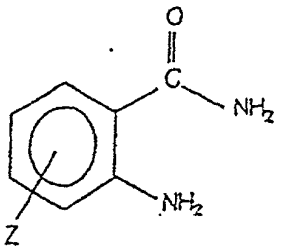
X is $-CH_2$, CO, or CS;

Y is S, NH, or $-(CH_2)_m-$;

n is 0 to 9

m is 1 to 4;

and a compounds of formula (II)



wherein

Z is $-OCH_3$, $-SO_3H$, $-SO_3^-M^+$, $-NO_2$, $-NH_2$, $-NH-NH_2$, $-CO_2^-M^+$, -CHO, or H

M is a cation;

wherein the molar ratio of amino resin former : formaldehyde : sulfite: nitrogen-containing formulation auxiliary is 1 : 1.9 – 6.0 : 1.0 – 2.0 : 0.01 – 1.5 and/or the molar ratio of naphthalene-sulfonic acid : formaldehyde : nitrogen-containing formulation auxiliary is 1 : 0.7 – 3.0 : 0.01 – 1.5.

14. A condensation product as claimed in claim 13, wherein said amino resin former is selected from the group consisting of melamine and urea.

15. A condensation product as claimed in claim 13, wherein said formulation auxiliary is selected from the group consisting of urea, thiourea, N-methylurea, 2-imidazolidinone and anthranilamide as formulation auxiliaries.

16. A condensation product as claimed in claim 13, wherein the amino resin former comprises up to 70% by weight of thiourea, dicyandiamide, a guanidine (salt) or mixtures thereof.

17. A condensation product as claimed in claim 13, wherein the condensation product is an aqueous solution having a solids content of from 20 to 60% by weight.

18. A condensation product as claimed in claim 17, wherein the viscosity of the aqueous solution at 95°C is from 0.5 to 250 $mm^2.s^{-1}$.

19. A condensation product as claimed in claim 13, wherein the aqueous solution has been dried to a residual moisture content of < 5%.

20. A process for preparing a condensation product as claimed in claim 13, comprising:

a) heating said amino resin former or formers, said formaldehyde and said sulfite component in a molar ratio of 1 : 1.9 – 6.0 : 1.0 – 2.0 in aqueous solution with addition of a portion of the selected molar amount of the formulation auxiliary at a temperature of from 40°C to 90°C and a pH of from 7.5 and 13.0 until sulfite is no longer detectable;

b) adding a portion 2 of the selected molar amount of the formulation auxiliary at a pH of from 3.0 to 7.0 and continuing the condensation at a temperature of from 60 to 95°C until the condensation product has a viscosity at 95°C of from 1 to 250 $mm^2.s^{-1}$;

c) adding the pH of condensation product to a pH of from 7.5 to 12.0 or conducting a thermal after-treatment at a pH of $\geq$ 10.0 and a temperature of from 65 to 90°C; and

d) adding a portion 3 of the selected molar amount of the formulation auxiliary;

wherein the sum of portion 1, portion 2 and portion 3 of the formulation auxiliary corresponds to the molar amount of the formulation auxiliary of the formula (I) and/ (II) and each individual portion can amount to a proportion of from 0 to 100 total-%, wherein portion 1 is < 100%.

21. The process as claimed in claim 20, wherein the resultant condensation products are dried in a spray drier or on a roller drier to a preferred residual moisture content of < 5% by evaporation of the water under reduced pressure.

22. A process for preparing a condensation product as claimed in claim 13, wherein the sulfonated melamine-formaldehyde condensation products, sulfonated melamine-urea-formaldehyde condensation products or naphthalenesulfonic acid-formaldehyde condensation products are admixed with from 0.1 to 50% by weight, based on the content of solid active components, of a formulation auxiliary of the formula (I) and (II) or mixtures thereof and dried to a residual moisture content of < 5%.

23.. An inorganic binders comprising from 0.01 to 20% by weight of condensation product as claimed in claim 13, based on the amount of the inorganic binders.

24. An hydraulically setting dry mixes comprising from 0.01 to 20% by weight, of a condensation product as claim in claim 13, based on the amount of inorganic binders.

REMARKS

Entry of this amendment is respectfully requested.

If any fees are due to enter this amendment or to maintain pendency of this application, please charge the fees to Deposit Account No. 50-0624.

Respectfully submitted

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(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
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(81) Bestimmungsstaaten *(national)*: CA, US.

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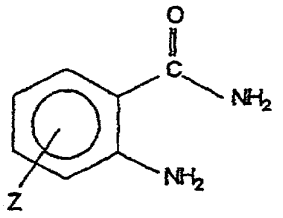
Veröffentlicht:
— *Mit internationalem Recherchenbericht.*

[Fortsetzung auf der nächsten Seite]

(54) Title: SULFONATED CONDENSATION PRODUCTS WHICH ARE STABILE IN STORAGE, METHOD FOR THE PRODUCTION THEREOF, AND THEIR USE

(54) Bezeichnung: LAGERSTABILE SULFONIERTE KONDENSATIONSPRODUKTE, VERFAHREN ZU IHRER HERSTELLUNG UND DEREN VERWENDUNG



(I)

(57) **Abstract:** The invention relates to sulfonated condensation products which are stabile in storage and which are based on aminoplastic formers comprising at least two amino groups or naphthalene and formaldehyde and, optionally comprising organic nitrogen bases which additionally contain, as nitrogenous formulation auxiliary agents, compounds of general formula (I) R^1-NH-X-Y-R^2, wherein R^1 and R^2, independent of one another, represent H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-(CH_2)_n-CH_2-$; X = $-CH_2$, CO, CS; Y = S, NH, $-(CH_2)_m-$; n = 0 to 9; m = 1 to 4; and/or compounds of general formula (II), wherein Z = $-OCH_3$, $-SO_3H$, $-SO_3^-Na^+$, $-NO_2$, $-NH_2$, $-NH-NH_2$, $-CO_2^-Na^+$, -CHO. According to the invention, the mol ratio of aminoplastic formers: formaldehyde: sulfite: nitrogenous formulation auxiliary agents equals 1: 1.9 to 6.0: 1.0 to 2.0: 0.01 to 1.5 and/or the mol ratio of naphthalene sulfonic acid: formaldehyde: nitrogenous formulation auxiliary agents equals 1: 0.7 to 3.0: 0.01 to 1.5. The invention also relates to a method for producing these condensation products and to their use, especially as additives for inorganic binding agents and for hydraulically setting dry mixtures that contain these inorganic binding agents. The inventive sulfonated condensation products which are stabile in storage are characterized, above all, by having a significantly increased thermal stability.

(57) **Zusammenfassung:** Gegenstand der vorliegenden Erfindung sind lagerstabile sulfonierte Kondensationsprodukte auf Basis Aminoplastbildner mit mindestens zwei Aminogruppen oder Naphthalin sowie Formaldehyd und ggf. organischen Stickstoffbasen, die zusätzlich als stickstoffhaltige Formulierungshilfsmittel Verbindungen der allgemeinen Formel (I): R^1-NH-X-Y-R^2, worin R^1 und R^2 unabhängig voneinander H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-(CH_2)_n-CH_2-$; X = $-CH_2$, CO, CS; Y = S, NH, $-(CH_2)_m-$; n = 0 bis 9; m = 1 bis 4; und/oder Verbindungen der allgemeinen Formel (II) worin Z = $-OCH_3$, $-SO_3H$, $-SO_3^-Na^+$, $-NO_2$, $-NH_2$, $-NH-NH_2$, $-CO_2^-Na^+$, -CHO, enthalten und bei denen das Mol-Verhältnis von Aminoplastbildner: Formaldehyd: Sulfit: stickstoffhaltigem Formulierungshilfsmittel 1: 1,9 bis 6,0: 1,0 bis 2,0: 0,01 bis 1,5 und/oder das Mol-Verhältnis von Naphthalinsulfonsäure: Formaldehyd: stickstoffhaltigem Formulierungshilfsmittel 1: 0,7 bis 3,0: 0,01 bis 1,5 beträgt. Beschrieben wird ferner ein Verfahren zur Herstellung dieser Kondensationsprodukte sowie deren Verwendung, insbesondere als Zusatzmittel für anorganische Bindemittel und für hydraulisch abbindende Trockenmischungen, die diese anorganischen Bindemittel enthalten. Insgesamt zeichnen sich die erfindungsgemäßen lagerstabilen sulfonierten Kondensationsprodukte vor allem durch eine signifikant erhöhte thermische Stabilität aus.

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Storage-stable sulfonated condensation products, process for preparing them and their use

Description

The present invention relates to storage-stable sulfonated condensation products, a process for preparing them and their use.

It is sufficiently known that hydraulically setting binders such as cement, lime, gypsum, $CaSO_4$ hemihydrates and anhydrites can be fluidized by addition of dispersants, which makes it possible to set desired low water/binder ratios. Classical dispersants which have been used for over 20 years are melamine-formaldehyde-sulfite (MSF) resins and naphthalenesulfonic acid-formaldehyde (NSF) resins which have been continuously developed further in recent years so as to be able to meet increased expectations.

Thus, DE 195 38 821 describes low-cost MFS resins containing a high proportion of sulfite. According to EP 690 083, a cost reduction is achieved by partial replacement of melamine by urea in a 2-stage process with addition of coreactants such as aminosulfonic acids, aminocarboxylic acids and caprolactam, etc., although this advantage is partly negated by an oxidation step to eliminate the excess sulfite.

Also customary is the addition of sulfanilic acid, as disclosed, for example, in DE 44 11 797 or in DE 196 09 614, in which case the sulfanilic acid is supplemented by polyoxyalkylene derivatives and/or aldehyde acid derivatives.

However, all these condensation products have the disadvantage that the spray drying of aqueous solutions

of conventional fluidizers has an extremely adverse effect on the early strength development which is of particular importance for $CaSO_4$ applications due to the high thermal stress during drying.

It is therefore an object of the present invention to develop storage-stable sulfonated condensation products based on an amino resin former having at least two amino groups and sulfite and/or naphthalenesulfonic acid together with formaldehyde which when used as additives for hydraulically setting additives do not display the abovementioned disadvantage of a thermal change but are instead stable over a wide temperature range.

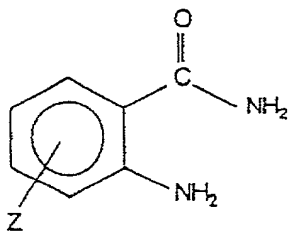
According to the invention, this object is achieved by sulfonated condensation products which further comprise at least one nitrogen-containing formulation auxiliary selected from among compounds of the formula (I)

$$R^1\text{-}NH\text{-}X\text{-}Y\text{-}R^2$$

where

R^1 and R^2		are each, independently of one another, H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-(CH_2)_n-CH_2-$
X	=	$-CH_2$, CO, CS
Y	=	S, NH, $-(CH_2)_m-$
n	=	0 to 9
m	=	1 to 4;

and/or compounds of the formula (II)



where

Z = $-OCH_3$, $-SO_3H$, $-SO_3^-M^+$, $-NO_2$, $-NH_2$, $-NH-NH_2$, $-CO_2^-M^+$, -CHO,

M = a cation, in particular Na

and in which the molar ratio of amino resin former : formaldehyde : sulfite : nitrogen-containing formulation auxiliary is 1 : 1.9 - 6.0 : 1.0 - 2.0 : 0.01 - 1.5 and/or the molar ratio of naphthalenesulfonic acid : formaldehyde : nitrogen-containing formulation auxiliary is 1 : 0.7 - 3.0 : 0.01 - 1.5.

Contrary to all expectations, it has been found that the storage-stable sulfonated condensation products of the invention display, in addition to the desired temperature stability, a drastic reduction in the undesirable outgassing of formaldehyde and/or ammonia which has hitherto been typical for this class of product. This effect displayed so clearly was not foreseeable.

As regards the components of the storage-stable sulfonated condensation products, the invention provides for melamine and/or urea to be used as preferred amino resin formers. These can be replaced to an extent of up to 70% by weight by thiourea, dicyandiamide, a guanidine (salt) and mixtures thereof, although ranges of from 30 to 50% by weight are to be preferred.

Likewise, urea and also thiourea, N-methylurea, 2-imidazolidinone and/or anthranilamide represent typical organic formulation auxiliaries for the purposes of the invention.

The nitrogen-containing formulation auxiliary can, if desired, be partly incorporated into the condensate of

amino resin former, formaldehyde and sulfite component or form an adduct with this.

For some applications, it has been found to be advantageous to use the condensation products as aqueous solutions. Aqueous solutions having a solids content of from 20 to 60% by weight and a viscosity at 95°C of from 0.5 to 250 $mm^2 \cdot s^{-1}$ are particularly useful for this purpose. On the other hand, the condensation products can also be used as dry products having a residual moisture content of < 5% (weight/weight).

Apart from the storage-stable sulfonated condensation products themselves, the present invention also claims a process for preparing them, in which

a) the amino resin former or formers, formaldehyde and the sulfite component are heated in a molar ratio of 1 : 1.9 - 6.0 : 1.0 - 2.0 in aqueous solution with addition of a portion 1 of the selected molar amount of the formulation auxiliary at a temperature of from 40°C to 90°C and a pH of from 7.5 and 13.0 until sulfite is no longer detectable,

b) a portion 2 of the selected molar amount of the formulation auxiliary is then added at a pH of from 3.0 to 7.0 and the condensation is continued at a temperature of from 60 to 95°C until the condensation product has a viscosity at 95°C of from 1 to 250 $mm^2 \cdot s^{-1}$,

c) the condensation product is subsequently brought to a pH of from 7.5 to 12.0 or a thermal after-treatment is carried out at a pH of ≥ 10.0 and a temperature of from 65 to 90°C and

d) a portion 3 of the selected molar amount of the formulation auxiliary is finally added,

where the sum of portion 1, portion 2 and portion 3 of the formulation auxiliary corresponds to the molar amount of the formulation auxiliary of the formula (I) and/or (II) and each individual portion can amount to a proportion of from 0 to 100 total-%, with the proviso that the portion 1 is < 100% and preferably < 99% and particularly preferably < 90%, respectively.

Furthermore, this process provides for the condensation products obtained in this way to be dried to a preferred residual moisture content of < 5%, which should preferably be carried out by evaporation of the water under reduced pressure, in a spray drier or on a roller dryer.

As an alternative method of preparing the condensation products claimed, it is proposed that sulfonated melamine-formaldehyde condensation products, sulfonated melamine-urea-formaldehyde condensation products or naphthalenesulfonic acid-formaldehyde condensation products be admixed with from 0.1 to 50% by weight, based on the content of solid active components, of a formulation auxiliary of the formulae (I) and/or (II) defined above or mixtures thereof and, if desired, dried to a residual moisture content of < 5%.

The storage-stable sulfonated condensation products are used either as additives for inorganic binders, e.g. cement, lime, gypsum, $CaSO_4$ hemihydrates and anhydrites, in an amount of from 0.01 to 20% by weight, based on the amount of the inorganic binders used, or else as additive for hydraulically setting dry mixes which comprise inorganic binders, in which case

preference is given to amounts of from 0.01 to 20% by weight, based on the amount of the inorganic binders used.

Overall, the storage-stable sulfonated condensation products of the invention represent a significant advance in respect of the thermal stability of these condensation products and also take account of the increased demands made of environmentally friendly products.

The following examples illustrate these advantages of the condensation products of the invention.

Examples

Example 1: (comparison, without formulation auxiliary)

332.1 g of formalin (30% strength), 156.5 g of water and 0.6 g of a 20% strength aqueous sodium hydroxide solution were placed in a round-bottom flask. 126.0 g of melamine were subsequently introduced, the solution was heated to 30°C and 121.3 g of sodium pyrosulfite and 16.5 g of 20% strength NaOH were added and the mixture was heated at 80°C until the sulfite is completely incorporated.
After the sulfite had been completely incorporated, 56.0 g of H_2SO_4 (10% strength) were added and condensation was then carried out at 80°C until the viscosity was 9.1 cSt; finally, 66.5 g of a 20% strength sodium hydroxide solution were added and the mixture was cooled to room temperature (RT).

The finished solution displayed the following physical data:

Solids content:	40.7% by weight
Viscosity:	3.40 cSt (20°C)
pH:	12.0

$HCHO_{free}$: 0.40%

This solution was dried in a spray drier to give a colorless powder; $HCHO_{free}$ content of the powder after drying: 0.22%.

Examples according to the invention: (with formulation auxiliary)

Example 2:

332.1 g of formalin (30% strength), 156.5 g of water and 0.6 g of a 20% strength aqueous sodium hydroxide solution were placed in a round-bottom flask. 126.0 g of melamine were subsequently introduced, the solution was heated to 30°C and 121.3 g of sodium pyrosulfite and 16.5 g of a 20% strength aqueous sodium hydroxide solution were added and the mixture was heated at 80°C until the sulfite is completely incorporated.

After the sulfite had been completely incorporated, 13.6 g of anthranilamide and 37.0 g of N-methylurea and also 56.0 g of H_2SO_4 (10% strength) and 25.3 g of water were added and condensation was carried out at 80°C until the viscosity was 9.1 cSt; finally, 20.9 g of a 20% strength sodium hydroxide solution were added and the mixture was cooled to RT.

The finished solution displayed the following physical data:

Solids content:	43.8% by weight
Viscosity:	2.89 cSt (20°C)
pH:	12.1
$HCHO_{free}$:	0.27%

This solution was dried in a spray drier to give a colorless powder; $HCHO_{free}$ content of the powder after drying: 0.19%.

Example 3:

332.1 g of formalin (30% strength), 156.5 g of water and 0.6 g of a 20% strength aqueous sodium hydroxide solution were placed in a round-bottom flask. 126.0 g of melamine were subsequently introduced, the solution was heated to 30°C and 121.3 g of sodium pyrosulfite and 16.5 g of a 20% strength aqueous sodium hydroxide solution were added and the mixture was heated at 80°C until the sulfite is completely incorporated.

After the sulfite had been completely incorporated, 56.0 g of H_2SO_4 (10% strength) were added and condensation was carried out at 80°C until the viscosity was 9.1 cSt; 13.6 g of anthranilamide, 25.8 g of 2-imidazolidinone and 20.1 g of water were then added and the solution was made alkaline by addition of 14.7 g of a 20% strength sodium hydroxide solution and cooled to RT.

The finished solution displayed the following physical data:

Solids content:	43.1% by weight
Viscosity:	3.10 cSt (20°C)
pH:	11.3
$HCHO_{free}$:	0.10%

This solution was dried in a spray drier to give a colorless powder; $HCHO_{free}$ content of the powder after drying: 0.08%.

Example 4:

332.1 g of formalin (30% strength), 156.5 g of water and 0.6 g of a 20% strength aqueous sodium hydroxide solution were placed in a round-bottom flask. 126.0 g of melamine were subsequently introduced, the solution was heated to 30°C and 121.3 g of sodium pyrosulfite and 16.5 g of a 20% strength aqueous sodium hydroxide solution and also 37.0 g of N-methylurea, 76.1 g of

thiourea and 150.6 g of water were added and the mixture was heated at 80°C until the sulfite is completely incorporated.

After the sulfite had been completely incorporated, 56.0 g of H_2SO_4 (10% strength) were added and condensation was carried out at 80°C until the viscosity was 3.9 cSt; finally, 22.2 g of a 20% strength sodium hydroxide solution were added and the mixture was cooled to RT.

The finished solution displayed the following physical data:

Solids content:	41.8% by weight
Viscosity:	2.53 cSt (20°C)
pH:	12.3
$HCHO_{free}$:	0.08%

This solution was dried in a spray drier to give a colorless powder; $HCHO_{free}$ content of the powder after drying: 0.07%.

Example 5:

332.1 g of formalin (30% strength), 156.5 g of water and 0.6 g of a 20% strength aqueous sodium hydroxide solution were placed in a round-bottom flask. 126.0 g of melamine were subsequently introduced, the solution was heated to 30°C and 121.3 g of sodium pyrosulfite and 16.5 g of a 20% strength sodium hydroxide solution and also 37.0 g of N-methylurea, 19.0 g of thiourea and 92.8 g of water were added and the mixture was heated at 80°C until the sulfite is completely incorporated.
After the sulfite had been completely incorporated, 56.0 g of H_2SO_4 (10% strength) were added and condensation was carried out at 80°C until the viscosity was 5.3 cSt; finally, 15.8 g of a 20% strength sodium hydroxide solution were added and the mixture was cooled to RT.

The finished solution displayed the following physical data:

Solids content:	40.5% by weight
Viscosity:	2.84 cSt (20°C)
pH:	12.0
$HCHO_{free}$:	0.10%

This solution was dried in a spray drier to give a colorless powder; $HCHO_{free}$ content of the powder after drying: 0.11%.

In the following, the properties of the resin-containing solutions and the powders produced therefrom were compared in an α-hemihydrate environment:

Basic formulation: 50.0 g of α-hemihydrate
16.0 g of water
0.180 g of the respective amino resin (calculated as solid)

Procedure:
The fluidized plaster slurries were poured from the mixing cup onto a glass plate in one action; after determining the spread (SP), setting was monitored by means of a Vicat needle about 1 cm from the edge of the gypsum plaster cake.

Results:

Examples	as solution		as powder		Δt of setting [min]
	SP [cm]	Setting [min]	SP [cm]	Setting [min]	
1 (comparison)	10.2	35	10.6	43	8
2	8.8	33	8.7	35	2
3	9.9	41	9.3	41	0
4	9.5	35	9.6	33	-2
5	9.8	35	9.9	33	-2

It can be seen that, in examples 2 to 4 according to the invention, setting of the gypsum plaster mix remains unchanged within the limits of accuracy when the solution has been spray dried to give a powder, while example 1 (comparison) without addition according to the invention of a formulation auxiliary displays a significantly prolonged setting time.

The same significant result can be seen in the change in the $HCOH_{free}$ values after drying (cf. examples 1 to 5). In example 1 (comparison) there is a relatively large decrease in the concentration of unreacted formaldehyde, while the resins of examples 2 to 4 according to the invention display excellent thermal stability during drying.

Claims

1. A storage-stable sulfonated condensation product based on an amino resin former having at least two amino groups and sulfite and/or naphthalenesulfonic acid and also formaldehyde and, if desired, organic nitrogen bases, characterized in that it comprises at least one nitrogen-containing formulation auxiliary selected from among compounds of the general formula (I)

$$R^1\text{-}NH\text{-}X\text{-}Y\text{-}R^2$$

where

R^1 and R^2 are each, independently of one another, H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-(CH_2)_n-CH_2-$

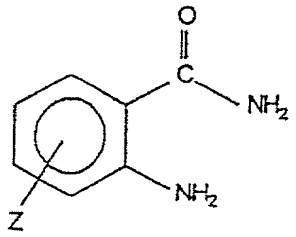
X = $-CH_2$, CO, CS

Y = S, NH, $-(CH_2)_m-$

n = 0 to 9

m = 1 to 4;

and/or compounds of the formula (II)



where

Z = $-OCH_3$, $-SO_3H$, $-SO_3^-M^+$, $-NO_2$, $-NH_2$, $-NH-NH_2$, $-CO_2^-M^+$, $-CHO$,

M = a cation

and in that the molar ratio of amino resin former : formaldehyde : sulfite : nitrogen-containing formulation auxiliary is 1 : 1.9 - 6.0 : 1.0 - 2.0 :

0.01 - 1.5 and/or the molar ratio of naphthalenesulfonic acid : formaldehyde : nitrogen-containing formulation auxiliary is 1 : 0.7 - 3.0 : 0.01 - 1.5.

2. A condensation product as claimed in claim 1, characterized in that it comprises melamine and/or urea as amino resin formers.

3. A condensation product as claimed in claim 1 or 2, characterized in that it comprises urea, thiourea, N-methylurea, 2-imidazolidinone and/or anthranilamide as formulation auxiliaries.

4. A condensation product as claimed in any of claims 1 to 3, characterized in that the amino resin former contains up to 70% by weight of thiourea, dicyandiamide, a guanidine (salt) and mixtures thereof.

5. A condensation product as claimed in any of claims 1 to 4, characterized in that it is in the form of an aqueous solution having a solids content of from 20 to 60% by weight.

6. A condensation product as claimed in claim 5, characterized in that the viscosity of the aqueous solution at 95°C is from 0.5 to 250 $mm^2 \cdot s^{-1}$.

7. A condensation product as claimed in any of claims 1 to 4, characterized in that it has been dried to a residual moisture content of < 5%.

8. A process for preparing a condensation product as claimed in any of claims 1 to 7, characterized in that

a) the amino resin former or formers, formaldehyde and the sulfite component are heated in a molar ratio of 1 : 1.9 - 6.0 : 1.0 - 2.0 in aqueous

solution with addition of a portion 1 of the selected molar amount of the formulation auxiliary at a temperature of from 40°C to 90°C and a pH of from 7.5 and 13.0 until sulfite is no longer detectable,

b) a portion 2 of the selected molar amount of the formulation auxiliary is then added at a pH of from 3.0 to 7.0 and the condensation is continued at a temperature of from 60 to 95°C until the condensation product has a viscosity at 95°C of from 1 to 250 $mm^2 \cdot s^{-1}$,

c) the condensation product is subsequently brought to a pH of from 7.5 to 12.0 or a thermal after-treatment is carried out at a pH of ≥ 10.0 and a temperature of from 65 to 90°C and

d) a portion 3 of the selected molar amount of the formulation auxiliary is finally added,

where the sum of portion 1, portion 2 and portion 3 of the formulation auxiliary corresponds to the molar amount of the formulation auxiliary of the formula (I) and/or (II) and each individual portion can amount to a proportion of from 0 to 100 total-%, with the proviso that the portion 1 is < 100%.

9. The process as claimed in claim 8, characterized in that the condensation products are dried to a preferred residual moisture content of < 5% by evaporation of the water under reduced pressure, in a spray drier or on a roller drier.

10. A process for preparing a condensation product as claimed in any of claims 1 to 7, characterized in that sulfonated melamine-formaldehyde condensation products, sulfonated melamine-urea-formaldehyde condensation

products or naphthalenesulfonic acid-formaldehyde condensation products are admixed with from 0.1 to 50% by weight, based on the content of solid active components, of a formulation auxiliary of the formula (I) and/or (II) or mixtures thereof and dried to a residual moisture content of < 5%.

11. The use of a condensation product as claimed in any of claims 1 to 7 as additive for inorganic binders in an amount of from 0.01 to 20% by weight, based on the amount of the inorganic binders used.

12. The use of a condensation product as claimed in any of claims 1 to 7 as additive for hydraulically setting dry mixes comprising inorganic binders, in an amount of from 0.01 to 20% by weight, based on the amount of inorganic binders used.

Abstract

The present invention relates to storage-stable sulfonated condensation products based on amino resin formers having at least two amino groups or naphthalene and also formaldehyde and, if desired, organic nitrogen bases, which further comprise, as nitrogen-containing formulation auxiliaries, compounds of the formula (I)

$$R^1\text{-}NH\text{-}X\text{-}Y\text{-}R^2$$

where

R^1 and R^2 are each, independently of one another, H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-(CH_2)_n-CH_2-$

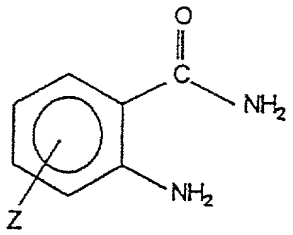
X = $-CH_2$, CO, CS

Y = S, NH, $-(CH_2)_m-$

n = 0 to 9

m = 1 to 4;

and/or compounds of the formula (II)



where

Z = $-OCH_3$, $-SO_3H$, $-SO_3^-N_2^+$, $-NO_2$, $-NH_2$, $-NH-NH_2$, $-CO_2^-Na^+$, -CHO,

and in which the molar ratio of amino resin former : formaldehyde : sulfite : nitrogen-containing formulation auxiliary is 1 : 1.9 - 6.0 : 1.0 - 2.0 : 0.01 - 1.5 and/or the molar ratio of naphthalenesulfonic acid : formaldehyde : nitrogen-containing formulation auxiliary is 1 : 0.7 - 3.0 : 0.01 - 1.5. Also described are a process for preparing

these condensation products and their use, in particular as additives for inorganic binders and for hydraulically setting dry mixes comprising these inorganic binders. Overall, the storage-stable sulfonated condensation products of the invention display, in particular, a significantly increased thermal stability.

ei/ANM/23208PWO September 22, 2000

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23208P US-WO

PTO/SB/01 (4-96)
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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☐ Declaration Submitted after Initial Filing

Attorney Docket Number	HUBR 1207
First Named Inventor	Holland, et al.
COMPLETE IF KNOWN	
Application Number	
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled :

Storage-stable sulfonated condensation products, process for preparing them and their use

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) September 29, 2000 as United States Application Number or PCT International Application Number PCT/EP00/09587 and was amended on (MM/DD/YYYY) Dec 14, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
199 46 591.6	Germany	Sept 29,99	☐	☐	☒
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
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☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	
		☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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DECLARATION — Utility or Design Patent Application

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

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Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])	Family Name or Surname
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Inventor's Signature	X Uwe Holland					Date	4/11/02
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City		State		ZIP		Country	

☒ Additional inventors are being named on the ___ supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

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DECLARATION

ADDITIONAL INVENTOR(S)
Supplemental Sheet

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City		State		Zip		Country	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	

Inventor's Signature: Date:

Residence: City		State		Country		Citizenship	

Post Office Address:

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